PATENT SPECIFICATION

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(54) ANTIPERSPIRANT PACKAGES

(71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised under the Laws of the State of Delaware, United States of Amreica, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to packages comprising pressurised antiperspirant compositions which are dispensable from valved aerosol containers and are deposited on the skin in powder form.

Because a dry powdered astringent or antiperspirant compound (e.g. aluminium chlorhydrate) expelled under pressure onto the human skin does not adhere satisfactorily to the skin, a vehicle is often present with the finely divided antiperspirant compound to help to maintain the powder on the skin after contact therewith. Such vehicles have usually been lipophilic materials which exhibit very little water solubility. These sometimes "insulate" the antiperspirant compound from contact with moisture on the skin and thereby delay the onset of astringent action. Because exuded perspiration becomes malodourous very quickly it is desirable to accelerate the dissolving of the antiperspirant compound rather than to delay this action. Yet, it remains important to hold the powdered material on the skin.

To promote dissolving of the antiperspirant compound and any hydration and hydrolysis that results, water-soluble vehicles may be employed. In some cases where nonionic surface active agents are used as vehicles it is found that their presence can have an irritating effect on the skin of some users. Additionally, some fatty and oily materials from sebum or perspiration and sometimes from compositions applied to the skin, may also be irritants and can cause staining of clothing contacted by antiperspirant compositions. It is desirable to alleviate such irritating effects and to make the stains readily removable or completely to avoid them, if possible.

According to the present invention there is provided a package which comprises a pressurised container containing an antiperspirant composition to be dispensed from the container as an aerosol, the composition comprising an antiperspirant compound in a proportion sufficient to have an effective antiperspirant action, a poly-lower alkoxylated cetyl alcohol in a proportion sufficient to act as a vehicle for the antiperspirant compound and to diminish irritation of the skin and staining of clothing, and a propellant fluid to maintain pressure in the container and to aid in discharging the composition therefrom.

The poly-lower alkoxylated cetyl alcohol promotes the solubilization of the antiperspirant compound and increases the mildness of the composition, tending to counteract any irritating effects, while simultaneously acting as a useful vehicle for applying the antiperspirant compound to the skin and making the composition non-staining. Any minor deposits on clothes are readily removed in washing, due to the presence in the deposits of the poly-lower alkoxylated cetyl alcohol.

In preferred forms of the invention the antiperspirant compound is aluminium chlorhydrate in finely divided powder form with particles in the 2 to 100 micron range, the poly-lower alkoxylated cetyl alcohol is polypropoxylated cetyl alcohol of about 10 propoxy groups per mole, the propellant fluid is a mixture of trichlorofluoromethane and dichlorodifluoromethane with the

former being present in major proportion thereof, and there are included in the composition a lower (C_1-C_4) aliphatic ester of a higher (C_{12}-C_{18}) fatty acid, such as isopropyl palmitate, a lower alkanol such as ethanol and a pyrogenic colloidal silica, such as that of particle sizes in the 0.1 to 2 micron range, sometimes sold under the trade mark "Cab-O-Sil."

Aluminium chlorhydrate, also sometimes called aluminium chlorhydroxide, has the formula $Al_2(OH)_5Cl.2H_2O$ and is available in finely powdered form, suitable for dispensing through the small valve openings of aerosol spray dispensers. Of course, it may be size-reduced as desired. For the present purposes particles of the aluminium chlorhydrate will be small, usually in the range from 1 to 1,000 microns, preferably 2 to 100 microns and most preferably averaging about 10 to about 50 microns in diameter or equivalent diameter.

To suspend the antiperspirant compound in particulate form and to produce a pressure in a dispensing container sufficient to discharge the antiperspirant compound particles when desired there is utilized a propellant fluid, preferably a lipophilic material in which antiperspirant compound is insoluble or only slightly soluble. Among the propellant fluids that are preferably used are the liquefied gases, materials which at atmospheric temperature and pressure will usually be in the gaseous state or can be vaporized readily at body temperature. Preferred useful propellants are liquefied gases, or mixtures thereof, of the hydrocarbon and/or halohydrocarbon types, preferably of 1 to 4 carbon atoms, with the halohydrocarbons having chlorine and/or fluorine as the halogen or halogens thereof. Particularly useful are mixtures of trichlorofluoromethane and dichlorodifluoromethane, for example those in which the proportion of the former to the later is approximately 2:1 or 65:35. However, other liquefied gas propellants of the hydrocarbon and halogenated hydrocarbon types may be employed in ratios appropriate to yield the desired dispensing pressure, which is normally from 10 to 100 psi (lbs/sq. in.), prepreferably 20 to 70 psi, more preferably 30 to 60 psi and often ideally about 50 psi. Such pressures are at 25°C. Among the propellants which may be employed are chlorodifluoromethane; dichlorodifluoromethane; difluoroethane; vinyl chloride; chlorodifluoroethane; dichlorotetrafluoroethane (asymmetrical); dichlorotetrafluoroethane (symmetrical); chlorotrifluoroethane; dichlorofluoroethane; "Chlorothene" ($CCl_3.CH_3$-CHLOROTHENE is a trade mark); and octafluorocyclobutane; all of which are examples of halogenated hydrocarbon propellants. Among the hydrocarbon propellants there may be mentioned propane; 2-methyl propane (isobutane); n-butane and cyclobutane. Other such propellants are discused in the text *Pressurized Packaging (Aerosols)* by Herzka and Pickthall (1958, Academic Press Inc., New York, U.S.A.) at pages 19-77. Although it is highly preferable to utilize the liquefied gases and compatible lipophilic solvents which are vaporizable at human skin temperature, one may also employ compressed gases, e.g. nitrous oxide, carbon dioxide or nitrogen, preferably mixed with a liquefied gas or gases. The liquefied propellants are preferred because they help to hold the antiperspirant compound in suspension and facilitate its being carried through valve restrictions during discharge.

With the antiperspirant compound-propellant fluid mix there is present a poly-lower alkoxylated cetyl alcohol vehicle in sufficient proportion to help the antiperspirant compound powder being dispensed to adhere to the skin area against which it is directed. The poly-lower alkoxylated cetyl alcohol should have such a lipophilic-hydrophilic balance as to be water-soluble and promote activation of the antiperspirant compound when it is on moist skin. Thus, when perspiration contacts the antiperspirant compound particles coated with poly-lower alkoxylated cetyl alcohol (or the mix of antiperspirant compound and pyrogenic silica particles coated with a mixture of hydrophilic poly-lower alkoxylated cetyl alcohol and higher fatty acid ester of lower alcohol) the alkoxylated material dissolves, and because of its hydrophilic and surface active properties promotes the contact of the antiperspirant compound with moisture and the consequent activation of the astringent product. Additionally, the poly-lower alkoxylated cetyl alcohol helps to remove greasy and oily stains from garments contacted with the present compositions, when such garments are washed. It has a soothing effect and counters irritation which may be caused to some sensitive skins by the presence of the antiperspirant compound or reaction products thereof or by the presence of perspiration, oily materials and other constituents of compositions applied to the skin.

The poly-lower alkoxylated cetyl alcohol is usually alkoxylated by propylene oxide but may have ethylene oxide present too. The extent of alkoxylation will generally be within the range of from 3 to 100 lower alkoxy groups per mole (lower meaning 2- to 3- carbon alkoxy groups) and of these, 10 to 100% will normally be propoxy, rather than ethoxy. The propoxy may be n-propoxy or isopropoxy. Preferred poly-

lower alkoxylated cetyl alcohols are completely water-soluble and will contain from 3 to 20 alkoxy groups per mole, often 5 to 15 and most preferably about 10 propoxy groups per mole. However, a balance can be struck between the proportion of ethoxy and propoxy groups and the length of the poly-lower alkoxy chain to produce a product of the most desired hydrophilic, water-soluble, counter-irritant, detersive and vehicle properties.

To help to hold the antiperspirant compound particles intimately suspended in the propellant—poly-lower alkoxylated cetyl alcohol solution (the alkoxylated alcohol is sufficiently propellant-soluble so as not to settle out on standing) a finely divided silica is preferably present. Such material also assists in maintaining a uniform coating of the antiperspirant compound on the skin and may also adsorb perspiration exuded despite the antiperspirant compound particles; yet it releases such perspiration to the antiperspirant compound to promote activation thereof. For best results the finely divided silica is a colloidal silica, preferably of the pyrogenic type, having a particle size in the 0.1 to 10 micron range, preferably of 0.1 to 2 microns. Such products are available under the trade mark "Cab-O-Sil", such as "Cab-O-Sil M-5". Of course, equivalents or substitutes may be employed providing that they have similar satisfactory properties.

With the hydrophilic polyalkoxylated cetyl alcohol it is desirable to employ a lesser quantity of a lipophilic vehicle to help to hold the antiperspirant compound on the skin and to facilitate a uniform distribution thereof. Vehicles of such desired properties are lower (C_1-C_4) aliphatic alcohol esters of higher (C_{12}-C_{18}) fatty acids. More preferably, the alcohols will be of 2 to 3 carbon atoms and the higher fatty acids will be of 14 to 18 carbon atoms. Most preferably, the alcohol is isopropanol and the fatty acid is palmitic acid. Thus, the lipophilic portions of both vehicles will be of 16 carbon atoms in the most preferred embodiments of the invention.

It is usually desirable, and sometimes very important, to have a co-solvent present in the composition in minor proportion to help to keep the lipophilic and hydrophilic vehicles uniformly distributed and to assist in maintaining them in such form that they are readily dispensed from the pressurized container when the valve thereof (it usually has a very small clearance) is opened. Further, it is desirable that a small proportion of volatilizable hydrophilic component be applied to the skin to help vaporize off from the skin upon contact some moisture which may be present thereon. This gives a slight cooling effect which ensures that the user will have a signal that the desired skin surface areas have been sufficiently covered with the antiperspirant composition. A useful co-solvent having the mentioned properties is a lower (C_1-C_4) aliphatic alcohol, preferably of 2 or 3 carbon atoms and most preferably ethanol. It is preferable that the alcohol be essentially water-free, as is also preferable for the entire composition.

Other antiperspirant materials can be substituted for aluminium chlorhydrate, for example, there may be employed astringents, e.g. aluminium, zirconium and zinc salts, such as aluminium chloride and aluminium sulphate.

Various adjuvants may be present in the antiperspirant compositions. Among these may be included bactericides, in permissible quantities; colourants, e.g. permitted dyes and pigments; perfumes, e.g. synthetic musk, natural odourants, and natural and synthetic floral perfumes; solvents, e.g. hydrocarbon oils and ethers; and nonionic surface active agents, e.g. nonyl phenyl polyoxyethylene ethanol of 10 oxyethylene groups per mole. Of course, such materials will be present only in proportions that are compatible with the other constituents and often none of these will be utilized except perfumes or odourants.

The proportions of the pressurized composition components employed are such as to result in the production of a dry spray of mild but effective non-staining antiperspirant. Generally the proportion of the antiperspirant compounds, e.g. aluminium chlorhydrate, is from 2 to 7%, preferably 2 to 4% and most preferably about 3% of the composition in the pressurized container. The propellant will usually be from 80 to 95% of the composition, preferably from 85 to 93% thereof and most preferably should be about 90%. The poly-lower alkoxylated cetyl alcohol is normally 2 to 9% of the composition, preferably 3 to 7% and most preferably about 3.8% thereof. The pyrogenic silica will usually be from 0.1 to 2%, preferably 0.2 to 1% and most preferably about 0.4% of the composition, and the auxiliary vehicle, such as a lower aliphatic alcohol ester of higher fatty acid, is from 0.5 to 3%, preferably from 0.5 to 1.5% and most preferably about 1% of the composition. The solvent, preferably a lower alkanol or a mixture thereof, generally constitutes from 0.5 to 5% of the composition, preferably 1 to 3% thereof and most preferably about 1.8%. The various adjuvants that may be employed can total up to as much as 20% of the composition, especially when an auxiliary solvent is present, but generally will not exceed 10% thereof and preferably not exceed 5%, with individual adjuvants usually being

limited to 2% and preferably to 1% of the composition.

The present compositions are well dispersed and may be characterized as homogeneous, requiring little agitation before use to make certain that the proportion of antiperspirant compound is constant during dispensing. The antiperspirant compound particles adhere well to the skin onto which they are sprayed and the compound is readily activated by contact with moisture on the skin. The compositions are non-staining and are mild to the skin with no irritation being noted. The effects described are attributable to the use of the particular poly-lower alkoxylated cetyl alcohol vehicles in conjunction with the antiperspirant compound and, in preferred embodiments, with the auxiliary solvent, vehicle and dispersing aid. When other higher fatty alcohols than cetyl alcohol are poly-lower alkoxylated the results obtained are not as satisfactory as those of the present invention and such is also sometimes the case when antiperspirant compounds other than aluminium chlorhydrate are employed. Similarly, when the higher fatty esters of lower alcohols are esters of fatty acids outside the ranges given (best results are obtained with the 16 carbon fatty acid) poor effects are obtained and when solvents and propellants other than those mentioned are used or when the alcohol solvent is omitted the products are not as good. Thus, it appears that the coaction of the mentioned ingredients is an important feature for the obtaining of the desired results mentioned.

The following Examples illustrate the invention. Unless otherwise mentioned, all parts and percentages and other ratios in the Examples and elsewhere throughout the specification are by weight and all temperatures are in °C.

EXAMPLE 1.

	Parts by weight
Aluminium chlorhydrate (powdered, of particle sizes in the 2 to 100 micron range, averaging about 10 microns)	3.0
Polypropoxylated cetyl alcohol (Procetyl AWS, manufactured by Croda, Inc. U.S.A.)	3.8
Pyrogenic silica (of particle sizes in the 0.1 to 2 micron range, sold as "Cab-O-Sil M-5" by Cabot Corporation, U.S.A.)	0.4
Isopropyl palmitate	1.0
Denatured ethyl alcohol (anhydrous)	1.8
Perfume	0.2
Propellant mixture, 65:35 trichlorofluoromethane; dichlorodifluoromethane	89.8

The above essentially anhydrous composition is made by adding each of the constituents to a valved dispensing container capable of being pressurized through the valve thereof, sealing the can and then adding the propellant mixture to it under pressure through the valve so as to obtain a final pressure of 50 psi. The package is sent to storage. After storage periods of as long as three months the product is tested *in vivo* and *in vitro* and it is found that the spray characteristics are uniform or substantially uniform throughout the entire life of the product. In any cases where there may be some inequality of spraying characteristics a light shaking of the container before discharging the antiperspirant composition helps to suspend the aluminium chlorhydrate more uniformly in the liquefied gas medium, together with the other parts of the composition, and produces the uniform spray characteristics desired.

When tested on human subjects (a panel of ten) it is found that the present composition is an efficient antiperspirant, significantly diminishig the amount of perspiration exuded (by proportions from 20 to 80%) and is non-irritating. Also, articles of clothing which come into contact with the areas to which the antiperspirant composition is applied are not stained by it and any slight deposits of fatty or oily materials, astringent and hydrolysis products thereof are readily removed upon normal washing. *In vitro* tests verify these conclusions.

On the contrary, when the Procetyl AWS is replaced by isopropyl myristate the compositions have a greater tendency to stain clothing and items of fabric onto which they are sprayed and such stains are not as readily removable during washing. When "Cab-O-Sil" is omitted from the formula the dispensing container should be shaken more vigorously before use to produce an evenly dispensed composition. If the isopropyl palmitate is omitted the composition is still useful but it appears that the aluminium chlorhydrate does not adhere as well to the skin onto which the composition is sprayed.

When proportions of the various constituents are modified so as to be outside the ranges described in the specification various detrimental effects are noted. For example, when the amount of aluminium chlorhydrate is diminished to outside the range its effect as an astringent is decreased and when more is employed significantly shorter bursts of spray (harder to control) are required and in some cases irritation may be apparent.

When too much of the poly-lower alkoxylated cetyl alcohol and the isopropyl palmitate or similar ester is used the com-

position may become sticky and may cause greasy staining of clothing, whereas when too little of these materials is employed the chlorhydrate does not get held satisfactorily to the skin onto which it is directed. Similarly, when the proportions of lower alkanol and/or propellant are outside the desired ranges the utilities of these materials are diminished. However, when variations in the constituents are made within the ranges given acceptable products having the useful characteristics recited above are obtained.

EXAMPLE 2

	Parts by weight
Aluminium chlorhydrate, powdered (with particle sizes of 2 to 100 microns)	3.0
Poly-lower alkoxylated cetyl alcohol (Procetyl AWS)	6.5
"Cab-O-Sil M-5"	0.4
Perfume	0.2
Propellant mixture (as in Example 1)	89.9

EXAMPLE 3

	Parts by weight
Aluminium chlorhydrate powder, finely divided	3.0
Polypropoxylated cetyl alcohol (averaging ten propoxy groups per mole)	4.5
Pyrogenic silica, "Cab-O-Sil" of particle sizes of about 0.5 micron	0.4
Perfume	0.2
Propellant mixture (2:1 trichlorofluoromethane: dichlorodifluoromethane)	91.9

In the compositions of Examples 2 and 3, which produce excellent powdered antiperspirants dispensable from an aerosol container of the type described in Example 1, various modifications in proportions and constituents are made in accordance with the teachings in this specification, with satisfactory antiperspirant compositions resulting. For example, in these formulations the polypropoxylated cetyl alcohol can be replaced with a corresponding alcohol containing from 30 to 60% of ethoxy groups, on a lower alkoxy molar basis, without interferring with the desirable activity of the composition. Also, the pyrogenic silica component is replaced by other colloidal silicas in the 0.1 to 10 micron range, preferably in the range of 0.1 to 2 microns, a wide variety of which is available on the market. Proportions of aluminium chlorhydrate are changed within the range of 2% to 7%, with the greater proportions being more actively astringent and antiperspirant, yet without irritation to normal skin. However, the aluminium chlorhydrate should not be changed to any other known astringent. Also readily changeable without affecting the properties of the composition is the propellants mixture, and any suitable combination of the propellants mentioned in the specification which yields a satisfactory dispensing pressure, usually from 10 to 100 psi and preferably from 20 to 70 psi, at 25°C, is useful. For example, mixtures of propane and isobutane may be employed.

EXAMPLE 4

	Parts by weight
Aluminium chlorhydrate powder (average particle size in the 10 to 40 micron range)	6.0
Polypropoxylated cetyl alcohol (as described in Example 1)	7.0
Isopropyl palmitate	1.0
Denatured ethanol (anhydrous)	1.8
"Cab-O-Sil M-5"	0.4
Perfume	0.2
Propellant mixture to generate 50 psi at 25°C (trichlorofluoromethane and dichlorodifluoromethane)	83.6

As with the previous compositions, that of this Example makes a satisfactory, adherent, long term effective, dry powdered antiperspirant composition, dispensable from a valved aerosol container. It is effective in diminishing perspiration and is non-irritating to normal skins. As is apparent from the increased content of aluminium chlorhydrate, less of the composition needs to be sprayed onto the skin to obtain an effect equivalent to those of the previous Examples.

WHAT WE CLAIM IS:—

1. A package which comprises a pressurised container containing an antiperspirant composition to be dispersed from the container as an aerosol, the composition comprising an antiperspirant compound in a proportion sufficient to have an effective antiperspirant action, a poly-lower alkoxylated cetyl alcohol in a proportion sufficient to act as a vehicle for the antiperspirant compound and to diminish irritation of the skin and staining of clothing, and a propellant fluid to maintain pressure in the container and to aid in discharging the composition therefrom.

2. A package according to Claim 1 wherein the antiperspirant compound is aluminium chlorhydrate in a proportion of from 2% to 7% of the composition.

3. A package according to Claim 2 wherein the aluminium chlorhydrate is in particulate form with particles in the 1 to 1000 micron range.

4. A package according to Claim 3 wherein the particulate aluminium chlorhydrate is in the 2 to 100 micron particle size range and constitutes from 2% to 4% of the composition.

5. A package according to Claim 4 wherein the particulate aluminium chlorhydrate constitutes about 3% of the composition.

6. A package according to any of the preceding claims wherein the poly-lower alkoxylated cetyl alcohol is at least partially propoxylated, containing from 10 to 100% propoxy groups, on a molar basis of lower alkoxy groups, with from 3 to 100 lower alkoxy groups per mole, and the proportion of lower alkoxylated cetyl alcohol in the composition is from 2 to 9%.

7. A package according to Claim 6 wherein the poly-lower alkoxylated cetyl alcohol is a completely water-soluble polypropoxylate of 3 to 20 propoxy groups per mole.

8. A package according to Claim 7 wherein the poly-lower alkoxylated cetyl alcohol is polypropoxylated cetyl alcohol of 5 to 15 propoxy groups per mole, and constitutes 3 to 7% of the composition.

9. A package according to Claim 8 wherein the polypropoxylated cetyl alcohol contains about 10 propoxy groups per mole and constitutes about 3.8% of the composition.

10. A package according to any of the preceding claims wherein the propellant fluid is a liquefied gas or a mixture of liquefied gases constituting from 80 to 95% of the pressurized composition, which creates a pressure of from 10 to 100 psi in the container at 25°C.

11. A package according to Claim 10 wherein the propellant fluid is a mixture of liquefied hydrocarbons, halohydrocarbons or both, which creates a pressure of from 20 to 70 psi in the container at 25°C.

12. A package according to Claim 11 wherein the propellant fluid is a mixture of halogenated hydrocarbon liquefied gases of from 1 to 4 carbon atoms, the halogens being chlorine and/or fluorine, and constitutes 85% to 93% of the composition, and creates a pressure of from 30 to 60 psi in the container at 25°C.

13. A package according to Claim 12 wherein the propellant fluid is a mixture of trichlorofluoromethane and dichlorodifluoromethane in approximately 2:1 ratio, and constitutes about 90% of the composition, and creates a pressure of approximately 50 psi in the container at 25°C.

14. A package according to any of the preceding claims wherein the composition includes as auxiliary constituents from 0.1% to 2% of pyrogenic colloidal silica of particle sizes in the 0.1 to 10 micron range, from 0.5% to 3% of a C_1-C_4 aliphatic alcohol ester of a C_{12}-C_{18} fatty acid and from 0.5% to 5% of an alkanol of 1 to 4 carbon atoms.

15. A package according to Claim 14 wherein the composition includes from 0.2% to 1% of pyrogenic colloidal silica of particle sizes in the 0.1 to 2 micron range, from 0.5% to 1.5% of a C_2-C_3 aliphatic alcohol ester of a C_{14}-C_{18} fatty acid and from 1% to 3% of a C_2-C_3 alkanol.

16. A package according to Claim 15 wherein the composition includes about: 0.4% of pyrogenic colloidal silica of particle sizes in the 0.1 to 2 micron range, 1% of isopropyl palmitate and 1.8% of anhydrous ethanol.

17. A package according to Claim 1 and substantially as described in any of the Examples.

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